Infrared Quantitative Analysis of Mixtures Containing Isopropenyl Stearate, Stearic Acid, Stearic Anhydride, and Mixed Stearic–Acetic Anhydride

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A method for the determination of individual components of complex mixtures is presented. The technique used is based on ir-absorbance measurements for stearic acid at 1700 and at 935 cm^{-1} when the concentration range exceeds 0.50% wt/vol; for isopropenyl stearate at 1145 and at 865 cm^{-1}; for stearic anhydride at 1030 cm^{-1} and mixed stearic-acetic anhydride at 1000 cm^{-1}. The baseline method was used in all absorbance measurements. Absorbance-concentration relationships obeyed Beer's law from 0 to 2.0% wt/vol for most compounds; the exception being stearic acid (at 1700 cm^{-1}), where linearity was limited to a maximum 0.50% wt/vol. Due to spectral interference between the two anhydrides at low concentration ratios, an empirical percent transmission ratio method was used to estimate the relative concentration of each. Binary and ternary systems were studied and the standard deviations of the differences between theoretical and calculated values indicate that this method is reliable.

INDEX HEADINGS: Quantitative infrared; Isopropenyl stearate; Base-line method.

INTRODUCTION

The utilization of inedible animal fats has become a major concern of the livestock industry. Because of their increased production and decided decrease in use, new areas of development must be found for marketing these fats.

An obvious solution to the problem would be the expanded use of fatty acids, or their derivatives. Enol esters, such as isopropenyl stearate (IPS), are useful intermediates capable of forming interesting derivatives of saturated fatty acids.[1] IPS is also an excellent reagent for the introduction of the long-chain acyl group into amides or imides. N-acylated products are formed from these otherwise hard to acylate compounds with little by-product contamination.[2] The development of an economically feasible process for the production of IPS should promote commercial interest and thus increase the utilization of long-chain fatty acids.

Such a process for synthesizing IPS from stearic acid (HST) and isopropenyl acetate (IPA) is being studied. The design, optimization, and scaleup of a process chemical reactor necessitated a study of the reaction mechanism and equilibria involved in this reaction. For this reason, a suitable method for determining the composition of mixtures obtained during this reaction was required. This paper reports on a procedure for the quantitative analysis of multicomponent mixtures based on infrared spectroscopy. Our study was confined to analyzing for the following components: stearic acid, isopropenyl stearate, stearic anhydride, and mixed stearic–acetic anhydride.

I. EXPERIMENTAL METHOD

A. Apparatus

Throughout this work a Perkin–Elmer[3] model 21 ir spectrophotometer equipped with a sodium chloride prism was employed. The instrument was calibrated with a polystyrene reference strip. Instrument settings were as follows: slit, standard program (slit widths at critical wave numbers listed in Table I); gain, 5.6; scan speed varied from 1000 to 80 cm^{-1}/min with an ideal speed between 125–150 cm^{-1}/min; suppression, 2.0; scale, 1× ordinate expansion; source current, 0.3 A.

A Gerber variable scale ruler was used to measure the percent transmission which was then converted to absorbance.

B. Reagents

Stearic acid (HST) was purchased from Humko Products, fractionally recrystallized from acetone and analyzed to be 99.73% pure HST. Isopropenyl stearate (IPS) was synthesized by the process under study,[4] purified by Florisil column chromatography and analyzed >99% IPS. Stearic anhydride (SA) was obtained as a by-product of this reaction, purified by crystallization from petroleum ether and analyzed >99% SA. A gas–liquid chromatographic (GLC)

Table 1. Spectroscopic data for individual compounds.

Compound	Absorption peak (cm^{-1})	Slit width[a] (mm)	Base line (cm^{-1})	Absorptivity 1% solution	r[b]
Stearic acid	1700[c]	0.075	1600–1800	0.960[c]	0.996
	935	0.184	850–1025	0.097	0.996
Isopropenyl stearate	1145	0.127	1025–1275	0.407	0.999
	865	0.222	850– 875	0.166	0.999
Stearic anhydride	1030	0.156	950–1200	0.447	0.998
Mixed anhydride	1000	0.165	950–1265	0.299	0.999

[a] Slit width at absorption peak.
[b] r is the correlation coefficients from linear regression.
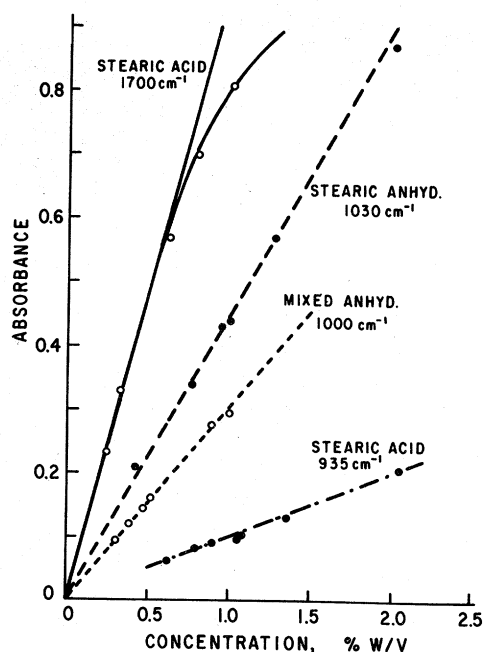[c] Absorbance–concentration relationship is a linear function from 0 to 0.50% wt/vol only.

FIG. 1. Plots of absorbance vs concentration for individual compounds.

procedure, as described by Luddy et al.,[5] was used to determine the above purities. CS_2 solutions of stearic acid and of isopropenyl stearate were analyzed directly to ascertain purity and as a further check their methyl esters were prepared and analyzed. Stearic anhydride, however, could only be analyzed as the methyl ester. All of these purified compounds were used in our standardization work.

Mixed stearic–acetic anhydride (MA) was synthesized by the above procedure[4] and purified by fractional crystallization from petroleum ether. The unstable nature of this compound prevented an analysis of its purity by the GLC technique. An ir spectrum of this purified compound was, however, compared with and found identical to a spectrum of an authentic mixed anhydride product previously reported by Rothman.[4] The absence of the 1030 cm⁻¹ band indicated that this compound was completely free of stearic anhydride. Therefore, this mixed anhydride was considered pure and was used in all our standardization work. As a precautionary measure solutions of this compound were prepared and immediately scanned to insure a minimum exposure to moisture.

All compounds were dissolved in carbon disulfide and the spectrum for each compound obtained from 4000 to 650 cm⁻¹, using a sodium chloride liquid cell with a pathlength of 0.402 mm.

II. RESULTS AND DISCUSSION

A. Individual Solutions

Preliminary examination of the spectrum of each compound revealed the existence of characteristic peaks (Table I) which could be used for quantitative determination.

Individual solutions of each compound, ranging in concentration from 0–2.0%, were prepared. The ir spectrum of each compound was obtained and absorbance measured at the selected wave numbers (Table I) using the base line method.[6] Absorbance versus concentration was plotted for each compound (Figs. 1 and 2). A linear regression was performed on these data and its significance determined by analysis of variance. The absorbance-concentration relationship for most compounds does obey Beer's law in this concentration range; an exception to this, however, is stearic acid at 1700 cm⁻¹. With HST the linearity of the absorbance–concentration relationship extended only to 0.50% wt/vol; beyond this concentration a curvilinear relationship was observed. Thus, when the absorbance of HST exceeds 0.500 absorbance units (approximately 0.5%) absorptivity cannot be used, instead the stearic acid concentration must be read directly from the calibration curve.

An alternative method for calculating stearic acid concentration at levels greater than 0.50% was to measure the 935 cm⁻¹ peak. Bonner and Hofstadter[7] associated this band only with dimer carboxyl group. Thus, this band does not appear in dilute solutions where the acid is entirely monomeric, but becomes increasingly more defined as concentration exceeds 0.50% wt/vol.

Absorptivities for a 1.0% solution of each compound are also shown in Table I and were utilized for converting absorbance to concentration.

B. Binary Systems

Having established the quantitative reliability of this infrared technique for individual standards, it was then necessary to ascertain the reliability of this technique for binary systems. Thus a series of binary mixtures were prepared (final concentration of 1.0%) and scanned as described above. The mixtures examined were isopropenyl stearate–stearic anhydride, isopropenyl stearate–mixed anhydride, stearic acid–stearic anhydride, and stearic anhydride–mixed an-
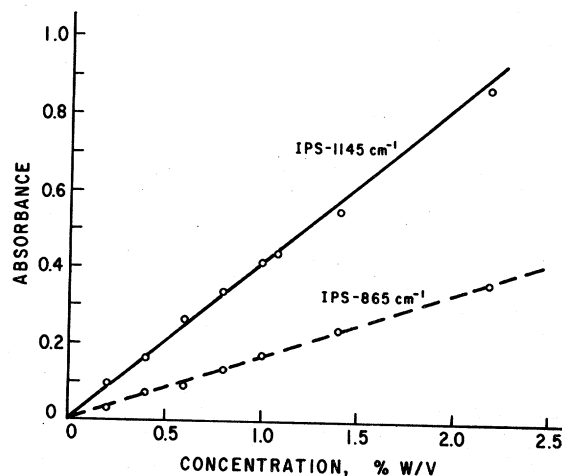

FIG. 2. Plots of absorbance vs concentration for isopropenyl stearate.

Table II. Infrared data for binary systems using the base line method.

Mixture	Isopropenyl stearate Theoretical Calculated mg/10 ml		Stearic anhydride Theoretical Calculated mg/10 ml		Mixed anhydride Theoretical Calculated mg/10 ml		Stearic acid[a] Theoretical Calculated mg/10 ml	
1	20.0	22.7			80.0	77.2		
	40.0	41.3			60.0	57.8		
	60.0	60.2			40.0	39.4		
	80.0	78.0			20.0	20.6		
					Std dev[b] = 1.6			
2	20.0	23.7	80.0	81.4				
	40.0	42.3	60.0	61.1				
	60.0	65.1	40.0	43.5				
	80.0	81.4	20.0	22.2				
	Std dev[b] = 2.6							
3			20.0	18.0			80.0	77.0[c]
			40.0	39.0			60.0	58.6[c]
			60.0	59.8			40.0	41.9
			80.0	79.8			20.0	22.6
			Std dev[b] = 1.6				Std dev[b] = 2.0	

[a] Using 1700 cm^{-1} peak.
[b] Standard deviation of the difference between theoretical and calculated values. Std dev $= \Sigma(\text{diff})^2/\text{No. of observations}$.
[c] Concentration read directly from calibration curve.

hydride. In all cases the sample mixtures were prepared as follows: individual 1.0% solutions were mixed in varying proportions 2.0, 8.0 ml; 4.0, 6.0 ml; 6.0, 4.0 ml; 8.0, 2.0 ml. The ir spectrum of each binary mixture was obtained and the absorbance for the individual compounds was measured using the baseline technique described above. Absorbance was then converted to concentration by utilizing the absorptivities obtained with single component systems. These data are plotted (Fig. 3) as the ratio of absorbances of the two compounds vs the ratio of their concentrations.[8] Linearity of three of these plots indicates direct correlation of absorbance vs concentration. Thus, Beer's law holds for each of the components of these binary systems and no interference is exhibited by

one absorption peak on another over the entire contration range studied (20.0–80.0 mg/10 ml).

The accuracy in determining concentration of these three binary systems using the baseline method is shown in Table II, where theoretical and calculated values are compared. The standard deviation of the difference between these values for each compound also is listed, and varies from 1.6 to 2.6 mg/10 ml.

The plot of the binary mixture consisting of stearic anhydride plus mixed anhydride (Fig. 3) appears to be a linear function but does not pass through the origin of the graph. Thus, the existence of spectral interference between the absorption peaks at relatively low concentration ratios is indicated. This interference prevented use of the direct baseline method for calculating concentration of each component. Therefore, to circumvent these difficulties an empirical percent transmission ratio method[9] was utilized in determining concentration. In this method we measured the percent transmission for each peak from a single base line (950–1265 cm^{-1}). For a given mixture the ratio of the percent transmission of the two anhydride peaks was obtained and plotted vs their relative proportion in the mixture (Fig. 4). To facilitate determining the relative proportion of each anhydride from
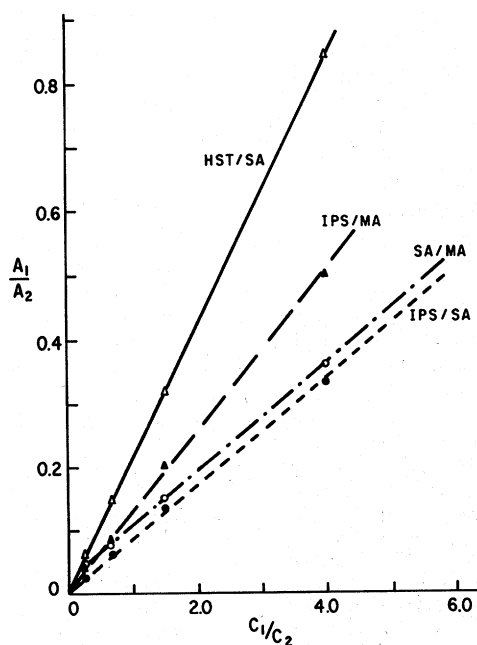

FIG. 3. Plots of compound ratios to test adherence to Beer's law.

Table III. Infrared data of ternary systems using the base line method and percent transmission ratio method.

Mixture	Mixed anhydride Theoretical Calculated mg/10 ml		Stearic anhydride Theoretical Calculated mg/10 ml		Isopropenyl stearate Theoretical Calculated mg/10 ml	
1	40.0	42.8	20.0	18.1	30.0	29.1
2	50.0	47.5	10.0	12.3	30.0	30.2
3	30.0	29.3	20.0	23.2	40.0	37.4
4	40.0	38.0	10.0	11.6	40.0	40.5
5	50.0	49.9	20.0	20.1	20.0	20.0
6	40.0	43.6	30.0	28.2	20.0	18.1
7	60.0	55.0	10.0	13.6	20.0	21.4
	Std dev[a] = 2.6		Std dev[a] = 2.1		Std dev[a] = 1.3	

[a] Standard deviation of the difference between theoretical and calculated values.

the curve shown in Fig. 4 an empirical quadratic equation ($X = 16.1Y^2 - 108.2Y + 167.8$), which fit the experimental data, was calculated. From these relative proportions the concentration of these two anhydrides in any system can be calculated by distributing the known weight accordingly. The reliability of this method for determining anhydride concentration is shown in Table III.

C. Ternary System

The final phase of this standardization study was carried out with the ternary system most likely to occur in the reaction under study. This system consisted of isopropenyl stearate, stearic anhydride, and mixed stearic–acetic anhydride. The original stearic acid was not included in this mixture because preliminary experiments showed depletion of this compound as the above listed reaction products formed.

The ternary mixtures were prepared by adding varying proportions of individual 1.0% solutions to a 10.0 ml volumetric flask so that the final concentration was always maintained at 90 mg solids/10 ml final volume. A typical scan of this ternary system is shown in Fig. 5.

Due to the known interference between mixed and stearic anhydride accurate estimation of these components was impossible by simply measuring individual peak heights. Therefore, it was necessary to divide the calculations into two steps. First, the concentration of IPS in the mixture was determined by measuring the absorbance of the 1145 cm^{-1} band (baseline 1010–1250 cm^{-1}) and calculating concentration using absorptivity. This calculated weight concentration of IPS was then subtracted from the total weight of sample in the system and the assumption made that the remaining weight concentration was
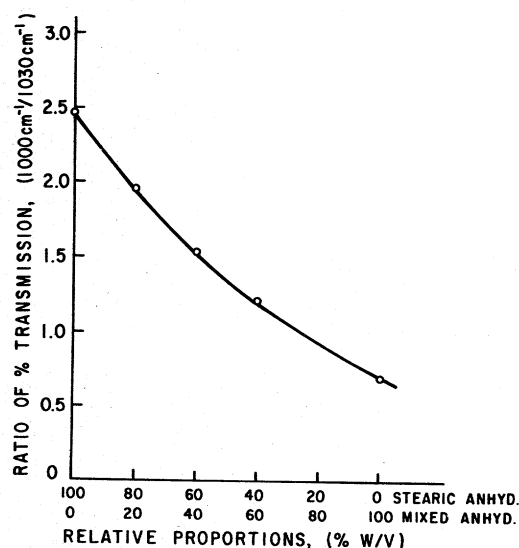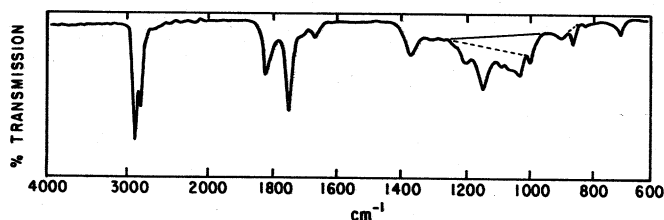

Fig. 5. Infrared spectrum of typical complex mixture.

distributed between the two anhydrides. Second, the percent transmission of each anhydride was measured from a single baseline (950–1265 cm^{-1}) and these values utilized in the empirical quadratic equation to obtain the relative proportions of the anhydrides. The remaining weight concentration was then distributed according to these relative proportions.

Data for the ternary system studied are shown in Table III. The results obtained demonstrate the reliability of the two-step procedure for calculating the composition of this ternary mixture. Also listed are the standard deviations of the differences between the theoretical and calculated values for the three compounds which range from 1.3 to 2.6 mg/10 ml.

III. CONCLUSION

It has been shown that this ir technique is satisfactory for the quantitative determination of single and multicomponent systems varying in concentration from 0.1 to 2.0% IPS, HST, SA, and MA. The standard deviations of the differences between theoretical and calculated values ranging from 1.3 to 2.6 mg/10 ml indicate the reliability of this method.

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Fig. 4. Plot of ratio percent transmission (1000 cm^{-1}/1030 cm^{-1}) vs relative proportions of anhydrides.